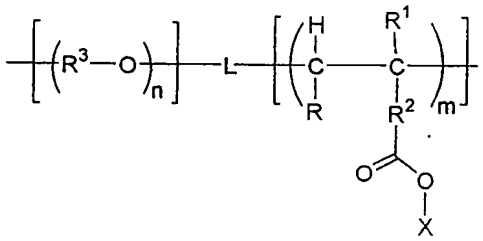
CLAIMS

1. A block copolymer comprising the unit (I)



(I)

wherein R is selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, carboxylic acid, C_2-C_{18} alkoxycarbonyl, C_2-C_{18} alkaminocarbonyl, or any one of C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, C_2-C_{18} alkoxycarbonyl and C_2-C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^1 is selected from the group consisting of hydrogen and C_1-C_6 alkyl groups; R^2 is a linking group; X is an electron withdrawing group; R^3 is selected from the group consisting of C_1-C_{18} alkylene, C_2-C_{18} alkenylene, C_7-C_{18} aralkylene, C_7-C_{18} alkarylene and C_6-C_{18} arylene; L is a divalent linker joining the blocks; and m and n are each an integer of greater than 1.

2. A block copolymer according to claim 1 in which m and n are integers of 5 to 300, more preferably 10 to 200, most preferably 25 to 150.

3. A block copolymer according to claim 1 or claim 2 which has a polydispersity of less than 1.4, preferably less than 1.2 and a molecular weight (Mw) of less than 100,000.

4. A block copolymer according to any preceding claim which is water soluble.

5. A block copolymer according to any preceding claim in which X is a carboxylate activating group, and is preferably selected from the group consisting of N-succinimidyl, pentachlorophenyl, pentafluorophenyl, para-nitrophenyl, dinitrophenyl, N-phthalimido, norbornyl, cyanomethyl, N-pyridyl, N-trichlorotriazine, 5-chloroquinilino, and N-imidazole, more preferably an N-succinimidyl or imidazole moiety.

6. A block copolymer according to any preceding claim in which R is selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_1-C_6 alkenyl, C_1-C_6 aralkyl and C_1-C_6 alkaryl, C_2-C_8 alkoxycarbonyl, C_2-C_8 alkaminocarbonyl, preferably hydrogen and methyl.

7. A block copolymer according to any preceding claim in which R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl or isomers thereof, preferably hydrogen and methyl.

8. A block copolymer according to any preceding claim in which R^2 is a bond or a divalent group selected from a carbonyl, C_1-C_{18} alkylene and/or C_6-C_{18} arylene group which may be substituted with 1 or more heteroatoms.

9. A block copolymer according to claim 8 in which R^2 is selected from the group consisting of C_1-C_6 alkylene, C_6-C_{12} arylene, C_1-C_{12} oxyalkylene and carbonyl-C_1-C_6 alkylene.

10. A block copolymer according to claim 9 in which R^2 is methylene, 1,2-ethylene, 1,3-propylene, hexylene, octylene, benzylene, tolylene or xylylene.

11. A block copolymer according to any preceding claim in which the groups R^3, which may be the same or different, are selected from the group consisting of C_1-C_8 alkylene groups, preferably 1,2-alkylene, and C_6-C_{12} arylene groups, most preferably methylene, ethylene, 1,2-propylene and 1,3-propylene.

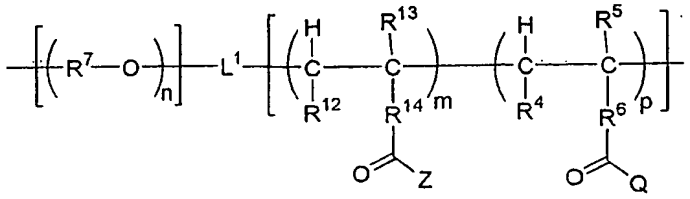
12. A block copolymer according to claim 11 in which all R^3 groups are the same and are preferably all 1, 2-ethylene or 1,2-propylene.

13. A block copolymer according to any preceding claim in which L comprises a C_1-C_{18} alkylene or C_6-C_{18} arylene group which may be substituted and/or interrupted with 1 or more heteroatoms.

14. A block copolymer according to claim 13 in which L is selected from the group consisting of C_1-C_6 alkylene, C_6-C_{12} arylene, C_1-C_{12} oxyalkylene and C_1-C_6 acyl.

15. A block copolymer according to claim 14 in which L comprises a -COR^a group, wherein R^a is selected from the group consisting of C_1-C_6 alkylene or C_6-C_{12} arylene, preferably methylene, 1,2-ethylene, 1,2-propylene, 1,3-propylene, ^{tert}butylene and ^{sec}butylene.

16. A block copolymer according to claim 1 which comprises the structure (II)



(II)

wherein R^4 is selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, carboxylic acid, C_2-C_{18} alkoxycarbonyl, C_2-C_{18} alkaminocarbonyl, or any one of C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, C_2-C_{18} alkoxycarbonyl, and C_2-C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^5 is selected from the group consisting of hydrogen and C_1-C_6 alkyl groups; R^6 is a linking group; Q is a solubilising group selected from the group consisting of hydroxyl, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_7-C_{12} aralkyl, C_7-C_{12} alkaryl, C_1-C_{12} alkoxy, C_1-C_{12} hydroxyalkyl, C_1-C_{12} alkylamino, C_1-C_{12} hydroxyalkylamino, or any of C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_7-C_{12} aralkyl, C_7-C_{12} alkaryl, C_1-C_{12} alkoxy, C_1-C_{12} hydroxyalkyl, C_1-C_{12} alkylamino, C_1-C_{12} alkylamino substituted with an amine, hydroxyl, carbonyl or thiol group; R^7 is selected from the group consisting of C_1-C_{18} alkylene, C_2-C_{18} alkenylene, C_7-C_{18} aralkylene, C_7-C_{18} alkarylene and C_6-C_{18} arylene; n, m and p are each an integer of greater than 1; R^{12} is selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, carboxylic acid, C_2-C_{18} alkoxycarbonyl, C_2-C_{18} alkaminocarbonyl, or any one of C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, C_2-C_{18} alkoxycarbonyl, and C_2-C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^{13} is selected from the group consisting of hydrogen and C_1-C_6 alkyl groups; R^{14} is a linking group; L^1 is a divalent linker joining the blocks; Z is a pendent group selected from the group consisting of $OM_{1/d}^{d+}$, NR^8R^9, SR^{10}, OR^{11} and OX, wherein X is defined above, M is a metal ion and

d is an integer of 1 or 2, R^8 comprises an alkyl group, preferably an aminoacyl substituted alkyl group, more preferably oligopeptidyl group; R^9 is selected from hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl; R^{10} and R^{11} comprise a group which is individually selected from the group consisting of hydrogen, C_1-C_{12} alkyl, C_2-C_{12} alkenyl, C_7-C_{12} aralkyl, C_7-C_{12} alkaryl and C_1-C_{12} hydroxyalkyl, and may contain one or more cleavable bonds and may comprise a bioactive agent.

17. A block copolymer according to claim 16 in which Z comprises one or more aminoacyl groups, preferably 2-6 aminoacyl groups, most preferably 4 aminoacyl groups.

18. A block copolymer according to claim 17 in which Z comprises a glycine-leucine-phenylalanine-glycine linker.

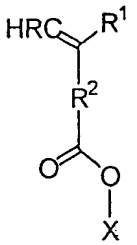
19. A block copolymer according to claim 16 in which Z comprises a cis-aconityl group.

20. A block copolymer according to any of claims 16 to 19 in which Z comprises a bioactive agent or linker.

21. A block copolymer according to claim 20 in which the bioactive agent is selected from anti-cancer agents.

22. A block copolymer according to any of claims 16 to 21 in which Q comprises an amine group attached to the R^6CO carbonyl carbon, preferably a C_1-C_{12} hydroxyalkylamino group, most preferably a 2-hydroxypropylamino group.

23. A process for the production of a block copolymer, comprising the polymerisation of ethylenically unsaturated monomers including a compound (III)

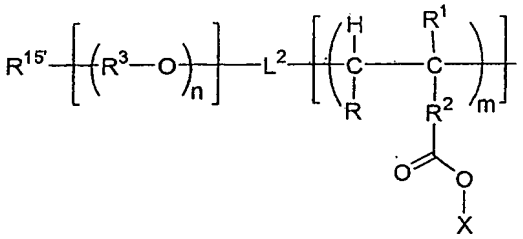


(III)

wherein R is selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, carboxylic acid, C_2-C_{18} alkoxycarbonyl, C_2-C_{18} alkaminocarbonyl, or any one of C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, C_2-C_{18} alkoxycarbonyl, and C_2-C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^1 is selected from the group consisting of hydrogen and C_1-C_6 alkyl groups; R^2 is a linking group; X is an electron withdrawing group; in the presence of an initiator compound (IV)

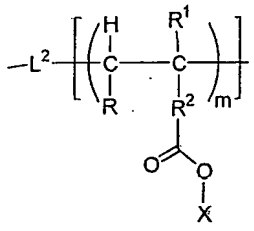
$$R^{15}(R^3O)_n\text{—}Y \qquad \text{(IV)}$$

wherein n is an integer of 1 or more and Y is a radical initiating group; R^3 is selected from the group consisting of C_1-C_{18} alkylene, C_2-C_{18} alkenylene, C_7-C_{18} aralkylene, C_7-C_{18} alkarylene and C_6-C_{18} arylene; R^{15} comprises a group selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl and C_6-C_{18} aryl, C_1-C_{18} alkoxy, C_2-C_{18} alkeneyloxy, C_7-C_{18} aralkoxy, C_7-C_{18} alkaryloxy, C_6-C_{18} aryloxy and -O-Y; to produce a block copolymer comprising the unit (V)



(V)

wherein m and n are as defined above and L^2 is a divalent linking group derived from Y and $R^{15'}$ is R^{15}, or where R^{15} is -O-Y, R^{15} is



24. A process according to claim 23 in which the groups X, R, R^1, R^2 and R^3 are as defined in any of claims 2 to 15.

25. A process according to claim 23 or 24 in which Y is a $-COR^y$ group, wherein R^y is selected from the group consisting of halogen substituted C_1-C_6 alkyl or C_6-C_{12} aryl, preferably methyl, ethyl, propyl, ^{tert}butyl and ^{sec}butyl preferably CO^{tert}butylbromide.

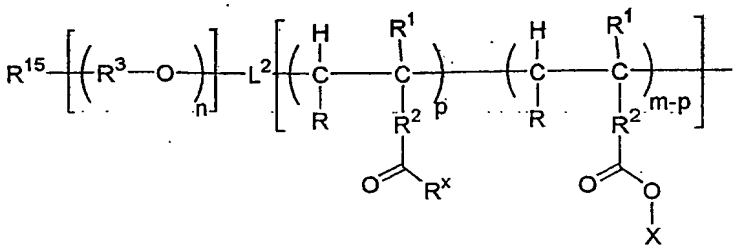
26. A process according to any of claims 23 to 25 in which L^2 is selected from the group consisting of C_1-C_6 alkylene, C_6-C_{12} arylene, C_1-C_{12} oxyalkylene and carbonyl-C_1-C_6 alkylene, preferably a $-COR^a$ group, wherein R^a is selected from the group consisting of C_1-C_6 alkylene or C_6-C_{12} arylene, preferably methylene, 1,2-ethylene, 1,2-propylene, 1,3-propylene, ^{tert}butylene and ^{sec}butylene.

27. A process according to any of claims 23 to 26 in which R^{15} is selected from hydrogen, C_1-C_6 alkyl, C_1-C_6 alkoxy, C_2-C_{10} alkenyl, C_7-C_{10} aralkyl, C_7-C_{10} alkaryl and C_6-C_{10} aryl and =O-Y, preferably methoxy or OY.

28. A process according to any of claims 23 to 27 which is a controlled radical polymerisation process, preferably an atom transfer radical polymerisation process, more preferably carried out in the presence of a polymerisation mediator comprising a Cu(I) complex.

29. A process according to any of claims 23 to 28 in which comonomers are copolymerised with the monomer of the formula III.

30. A process according to any of claims 23 to 29 in which the block copolymer of the formula V is reacted further with a reagent HR^x, wherein R^x is selected from the group consisting of $NR^{19}R^{20}$, SR^{21} and OR^{22}, wherein R^{19} is or comprises a linker group, preferably a substituted alkyl group, more preferably a peptidic group; R^{20} is selected from hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl; R^{21} and R^{22} are selected from the group consisting of hydrogen, C_1-C_{12} alkyl, C_1-C_{12} alkenyl, C_1-C_{12} aralkyl, C_1-C_{12} alkaryl, C_1-C_{12} alkoxy and C_1-C_{12} hydroxyalkyl, any of which may comprise a bioactive agent substituent and/or may contain one or more cleavable bonds, to form a derivatised block copolymer having the structure (VI)



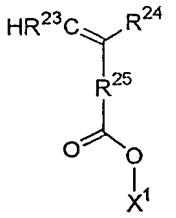
(VI)

wherein $1 \leq p \leq m$.

31. A process according to claim 30 in which HR^x is H_2NR^2 in which R^2 comprises an aminoacyl linker or a cis-aconityl linker and a bioactive agent or a ligand.

32. A process according to claim 30 or 31 in which the block copolymer of the formula VI is quenched by reacting remaining groups -COOX with an amine-group-containing compound, preferably hydroxypropylamine.

33. A process for the production of a block copolymer, comprising the steps of (39) polymerising ethylenically unsaturated monomers comprising a compound (VIII)



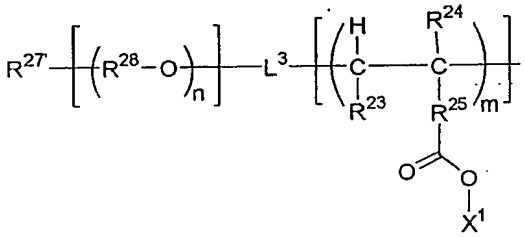
(VIII)

wherein R^{23} is selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, carboxylic acid, C_2-C_{18} alkoxycarbonyl, C_2-C_{18} alkaminocarbonyl, or any one of C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl, C_2-C_{18} alkoxycarbonyl, and C_2-C_{18} alkaminocarbonyl substituted with a heteroatom within, or attached to, the carbon backbone; R^{24} is selected from the group consisting of hydrogen and C_1-C_6 alkyl groups; R^{25} is a linking group; X^1 is selected from the group consisting of carboxyl activating groups, hydrogen, $M^1_{1/d}{}^{d+}$ and carboxyl protecting groups, wherein M^1 is a metal ion and d is an integer of 1 or 2; R^{26} is selected from the group consisting of C_1-C_{18} alkylene,

C_2-C_{18} alkenylene, C_7-C_{18} aralkylene, C_7-C_{18} alkarylene and C_6-C_{18} arylene; in the presence of an initiator compound (VIII)

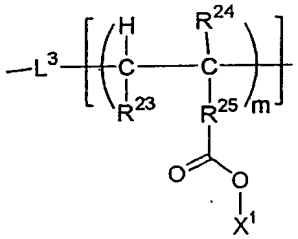
$$R^{27}(R^{28}O)_n—Y^1 \qquad (IX)$$

wherein n is an integer of 1 or more and Y^1 is a radical initiating group, R^{27} comprises a group selected from the group consisting of hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl and C_6-C_{18} aryl, C_1-C_{18} alkoxy, C_2-C_{18} alkeneyloxy, C_7-C_{18} aralkoxy, C_7-C_{18} alkaryloxy, C_6-C_{18} aryloxy and -O-Y^1; and R^{28} is selected from the group consisting of C_1-C_{18} alkylene, C_2-C_{18} alkenylene, C_7-C_{18} aralkylene, C_7-C_{18} alkarylene and C_6-C_{18} arylene; to produce a block copolymer comprising the unit (X)



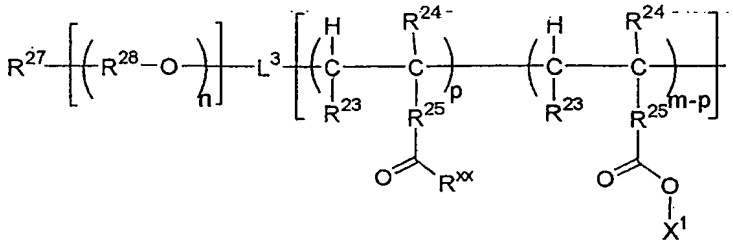
(X)

wherein m is an integer of greater than 1 and L^3 is a divalent linking group derived from L^3; and $R^{27'}$ is R^{27}, or where R^{27} is -O-Y^1, R^{27} is



39. reacting (X) with a reagent HR^{xx}, wherein R^{xx} is selected from the group consisting of $NR^{29}R^{30}$, SR^{31} and OR^{32}, wherein R^{29} is a linker group, preferably a peptidic group; R^{30} is selected from hydrogen, C_1-C_{18} alkyl, C_2-C_{18} alkenyl, C_7-C_{18} aralkyl, C_7-C_{18} alkaryl, C_6-C_{18} aryl; R^{31} and R^{32} are individually selected from the group consisting of hydrogen, C_1-C_{12} alkyl, C_1-C_{12} alkenyl, C_1-C_{12} aralkyl, C_1-C_{12} alkaryl, C_1-C_{12} alkoxy and C_1-C_{12}

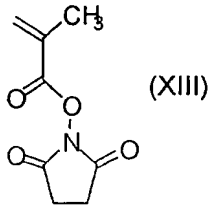
hydroxyalkyl, and may contain one or more cleavable bonds, to form a derivatised block copolymer having the structure (XI)



(XI)

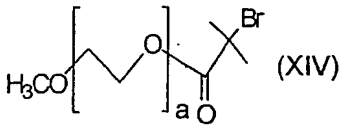
wherein $1 \leq p \leq m$.

34. A process according to claim 23 or claim 33 in which the ethylenically unsaturated monomer compound is



(XIII)

and the initiator is



(XIV)

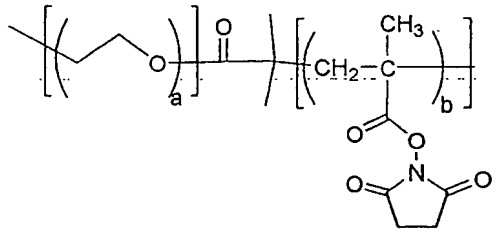
in which a is 1 to 500.

35. A process according to claim 34 in which the copolymer is reacted with a compound

H_2N-Gly-Len-Phe-Gly-Doxorubicin

and in which the product is reacted with 2-hydroxy-propylamine.

36. A block copolymer according to any of claims 1 to 22 having the structure (XII)



(XII)

wherein a and b are integers of up to 500.

37. A block copolymer which is obtainable by reaching the block copolymer of claim 36 and a reagent selected to provide a pendant group comprising an aminoacyl linker or a cis-aconityl linker and a bioactive agent.